XII. *The Function of Osmotic Pressure in the Analogy between Solutions and Gases.* *By* Professor J. VAN'T HOFF[*].

DURING an investigation which required some knowledge of the laws regulating chemical equilibrium in solutions, the conclusion has gradually been evolved that a deep analogy —indeed almost an identity—exists between dilute solutions exerting osmotic pressure on the one hand, and gases under ordinary atmospheric pressure on the other. The following pages contain an attempt to explain this analogy; and the physical properties of such systems will form the first subject of discussion.

### I. *Osmotic Pressure—the nature of the Analogy due to this conception.*

In order clearly to realize the quantity referred to as osmotic pressure, imagine a vessel, A (fig. 1), completely full of an aqueous solution of sugar, placed in water, B. If it be conceived that the solid walls of this vessel are permeable to water, but impermeable to the dissolved sugar, then, owing to the attraction of the solution for water, water will enter the vessel A up to a certain limit, thereby increasing the pressure on the walls of the vessel. Equilibrium then ensues, owing to the pressure resisting further entry of water. This pressure we have termed *osmotic pressure*.

Fig. 1.
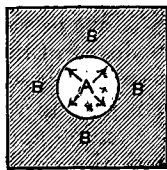
[*] Communicated to the Physical Society; translated by Prof. W. Ramsay, F.R.S.: read June 9, 1888.

It is evident that this state of equilibrium might have been attained in A without entry of water if the vessel had been constructed with a piston, compressing the solution with a pressure equal to the osmotic pressure (fig. 2). It follows moreover

Fig. 2.
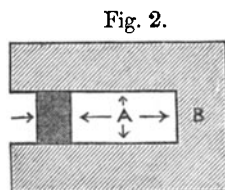
that, by increasing or diminishing the pressure on the piston, the state of concentration of the liquid can also be altered, owing to the passage of water through the walls of the vessel in an outward or inward direction.

Such osmotic pressure has been experimentally investigated by Pfeffer (*Osmotische Untersuchungen*, Leipsig, 1887). The walls of the cell consisted of unglazed porcelain, rendered impermeable to sugar though not to water, by filling it with a solution of potassium ferrocyanide and placing it in a solution of copper sulphate. Owing to diffusion, the ferrocyanide and the copper-salt come in contact after some time, and produce a membrane of copper ferrocyanide having the required properties. Such a vessel is then filled with a one-per-cent. solution of sugar ; it is then closed with a cork provided with a manometer, and sunk in water ; the osmotic pressure gradually rises, owing to entry of water, and the pressure due to the entry of water is read off when it becomes constant. As an example of the results obtained, it may be mentioned that a one-per- cent. solution of sugar (which, owing to its considerable mass, was not appreciably diluted on entry of water) exerted at $6°·8$ a pressure of $50·5$ millim. of mercury—about one fifteenth of an atmosphere.

The porous membrane, such as that described, will be termed in the following pages a "semipermeable membrane;" and the conception will be made use of even where experimental verification is lacking. The behaviour of solutions may thus be studied in a manner strikingly analogous to that employed in the study of gases, inasmuch as what is known as "osmotic pressure" corresponds to pressure, or, as it is commonly but incorrectly termed, "tension" of a gas. It is right to mention that this is no fanciful analogy, but a fundamental one ; the mechanism which, according to our present views, controls the pressure of gases and the osmotic pressure of liquids is substantially the same. In the former case pressure is due to the impacts of gaseous molecules on the walls of the containing vessel, and in the latter to the impacts of the molecules of the dissolved substance on the semipermeable membrane, since the impacts of the molecules of the solvent, being equal and opposed on each side of the vessel, may be neglected.

The great practical advantage arising from this method of regarding the behaviour of solutions, which leads at once to quantitative conclusions, consists in the fact that the application of the second law of thermodynamics to liquids is rendered exceedingly easy ; for reversible processes, of which this law treats, can now be very simply conceived. It has already been mentioned that a piston and cylinder with semipermeable walls, placed in the solvent, permits of alteration of concentration of the solution contained therein, by alteration of the pressure on the piston, in exactly the same way as a gas can be rarefied or compressed; except that in the former case it is the solvent which escapes through the semipermeable walls on increase of pressure. Processes of this kind can always be made reversible, if care be taken that the pressure on the piston is made equal to the opposed pressure, that is, in the case of solutions, the osmotic pressure.

We shall make use of this practical advantage in the following pages, particularly in investigating the laws of " ideal solutions;" that is to say, solutions so dilute as to be comparable with " ideal " or " perfect " gases, in which the action on one another of the dissolved molecules, as well as their actual volume compared with that of the space they inhabit, is so small as to be negligible.

II. Boyle's *Law for Dilute Solutions.*

The analogy between dilute solutions and gases acquires at once a quantitative form, if it be noted that in both cases alteration of concentration exercises a similar influence on pressure, and is in both cases proportional to the pressure.

This proportionality, which for gases goes by the name of Boyle's law, may be proved experimentally for liquids, as well as deduced theoretically.

Experimental Proof (Determination of osmotic pressure for solutions of various concentrations).—Let us first adduce Pfeffer's determinations (*Osmotische Untersuchungen*, p. 71) of the osmotic pressure (P) in sugar-solutions at the same temperature ($13°\cdot2$ to $16°\cdot1$), and with varying concentrations (C):—

C.	P.	$\dfrac{P}{C}$.
1 per cent.	535 millim.	535
2 ,,	1016 ,,	508
2·74 ,,	1518 ,,	554
4 ,,	2082 ,,	521
6 ,,	3075 ,,	513

The approximately constant quotients $\dfrac{P}{C}$ point conclusively to this proportionality between pressure and concentration.

Comparison of Osmotic Pressures by Physiological Methods. —Observations of de Vries ("Eine Methode zur Analyse der Turgorkraft," Pringsheim's *Jahrb.* xiv.) show that equal changes of concentration of solutions of sugar, and of potassium sulphate and nitrate, exercise equal influence on the osmotic pressure. This osmotic pressure was compared, by physiological methods, with that of the contents of a plant-cell ; the protoplasmal envelope contracts when it is immersed in solutions possessing great attraction for water. By a systematic comparison of the three bodies mentioned, using the same cells, three *isotonic liquids* (*i. e.* liquids exhibiting the same osmotic pressure) were obtained. Cells of a different plant were then made use of, and so four *isotonic* series were constructed which showed a similar proportion in their concentrations ; this is exhibited in the following table, where the concentrations are expressed in gram-molecules per litre :—

Series.	KNO_3.	$C_{12}H_{22}O_{11}$.	K_2SO_4.	$KNO_3=1$.	$C_{12}H_{22}O_{11}$.	K_2SO_4.
I. .	0·12	—	0·09	1	—	0·75
II. .	0·13	0·2	0·1	1	1·54	0·77
III. .	0·195	0·3	0·15	1	1·54	0·77
IV. .	0·26	0·4	—	1	1·54	—

Theoretical Proof.—These observations render highly probable the existence of proportionality between osmotic pressure and concentration, and the theorem may be completed by a theoretical proof which is, indeed, almost self-evident. Regarding osmotic pressure as due to a kinetic cause (*i. e.* as produced by impacts of the dissolved molecules), there must exist a proportionality between the number of impacts in unit time and the number of molecules in unit volume. The proof is therefore exactly the same as that for Boyle's law. If, on the other hand, osmotic pressure be regarded as the outcome of an attraction for water-molecules, its value is evidently proportional to the number of attracting molecules in unit volume, provided (and this is taken for granted in sufficiently dilute solutions) the dissolved molecules exercise no attraction on each other, and each one exerts its own special attractive action, uninfluenced by its neighbours.
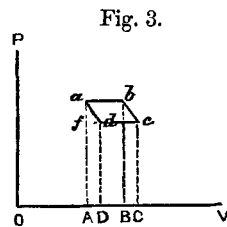
III. Gay-Lussac's *Law for Dilute Solutions.*

While the proportionality between concentration and osmotic pressure is self-evident, so long as temperature remains

constant, the proportionality between osmotic pressure and absolute temperature, the concentration being maintained constant, is not so manifest. Yet proof can be furnished from thermodynamical considerations ; and experimental data exist which are highly favourable to the results predicted on thermodynamical grounds.

Theoretical Proof.—It has been already mentioned that, by means of a piston and a cylinder with semipermeable walls, reversible processes can be conceived to occur. If such processes are expressed in the way common as regards gases, volume and pressures are indicated on the lines O V and O P (fig. 3); but pressure in this case, as before, must be taken as osmotic pressure. The initial volume (V cub. metres) is represented by OA ; the initial pressure on the piston of area 1 square metre (P kilogr.) by Aa; and the absolute temperature by T ; the solution is then conceived to undergo a minute increase of volume,

Fig. 3.

dV cubic metres (=AB), by moving the piston through dV metres, while the temperature of the solution is maintained constant by introduction of the requisite amount of heat. This amount of heat can be at once determined, inasmuch as it is equivalent to the external work performed, PdV, by the motion of the piston. Internal work is absent, for the dilution is, by hypothesis, so great that the dissolved molecules exercise no attraction on each other   This isothermal change ab is succeeded by the isentropic or adiabatic change bc, during which heat is neither absorbed nor evolved ; the temperature sinks by dT° ; and the original condition is then brought about by a second isothermal and a second adiabatic change, cd and da, respectively. The second law of thermodynamics requires that the fraction, $\dfrac{d\mathrm{T}}{\mathrm{T}}$ PdV of the initially imparted heat charge PdV shall have been converted into work ; this must be equivalent to the area $abcd$; and hence the equation follows: $\dfrac{d\mathrm{T}}{\mathrm{T}}$ PdV $= a\,b\,c\,d = af$. AB $= af\,d$V ; and hence P$\dfrac{d\mathrm{T}}{\mathrm{T}} = af$. But af represents the change of osmotic pressure, volume being kept constant, due to the change of temperature dT ; *i. e.* $\left(\dfrac{d\mathrm{P}}{d\mathrm{T}}\right)_v d\mathrm{T}$; hence

$$\left(\frac{d\mathrm{P}}{d\mathrm{T}}\right)_v = \frac{\mathrm{P}}{\mathrm{T}}.$$

On integration this equation gives, on the assumption of constant volume,

$$\frac{P}{T} = \text{constant};$$

that is, the osmotic pressure is proportional to the absolute temperature, provided concentration (which is here equivalent to the volume of a gas) remain constant ; and this is entirely in accordance with Gay-Lussac's law connecting the pressure and temperature of gases.

Experimental Proof (Determination of the osmotic pressure at different temperatures).—Let us compare this theoretical conclusion with the experimental data furnished by Pfeffer (pp. 114-115). He found that the osmotic pressure increases with rise of temperature ; it will be seen that, although his results do not furnish a conclusive proof of the correctness of the theorem, yet there is a most striking correspondence between experiment and theory. If we calculate from one of two experiments at different temperatures the osmotic pressure to be expected in the other, by help of Gay-Lussac's law, and compare it with the experimental result, we have the following series :—

1. Solution of cane-sugar.
     Pressure at 32°, found . . . 544 millim.
     Pressure at 14°·15, calculated . 512   ,,
         ,,   ,,   found . . 510   ,,
2. Solution of cane-sugar.
     Pressure at 36°, found . . . 567   ,,
     Pressure at 15°·5, calculated . 529   ,,
         ,,   ,,   found . . 520·5 ,,
3. Solution of sodium tartrate.
     Pressure at 36°·6, found . . 1564   ,,
     Pressure at 13°·3, calculated . 1443   ,,
         ,,   ,,   found . . 1431·6 ,,
4. Solution of sodium tartrate.
     Pressure at 37°·3, found . . 983   ,,
     Pressure at 13°·3, calculated . 907   ,,
         ,,   ,,   found . . 908   ,,

Comparison of the Osmotic Pressure by Physiological Methods.—In the same manner that support has been lent to the application of Boyle's law to solutions (viz. that different substances in *isotonic* solutions retain their equality of osmotic pressure so long as their respective concentrations are reduced to the same fraction), so the application of Gay-Lussac's law receives support by the fact that this isotonic

state is maintained during equal alterations of temperature. It has been proved by physiological methods by Donders and Hamburger (*Onderzoekingen gedaan in het physiologisch. Laboratorium der Utrechtsche Hoogeschool* [3] ix. p 26), making use of blood-corpuscles, that solutions of potassium nitrate, sodium chloride, and sugar, which at 0° are isotonic with the contents of these cells, and hence are isotonic with each other, exhibit the same isotonic state at 34°; this is seen in the annexed table :—

		Temperature 0°.	Temperature 34°.
KNO_3	. .	1·052 to 1·03 p. c.	1·052 to 1·03 p. c.
NaCl	. . .	0·62 to 0·609 p. c.	0·62 to 0·609 p c.
$C_{12}H_{22}O_{11}$	. .	5·48 to 5·38 p. c.	5·48 to 5·38 p. c.

Experimental Proof of Boyle's *and* Gay-Lussac's *Laws for Solutions. Experiments by* Soret (*Archives des Sciences phys. et nat.* [3] ii. p. 48 ; *Ann. Chim. Phys.* [5] xxii. p. 293).— The phenomenon observed by Soret lends a strong support to the analogy between dilute solutions and gases in respect of the influence of concentration and temperature on pressure. His work shows that just as in gases the warmest part is the most rarefied, so with solutions the warmest portions are the most dilute ; but that in the latter case a much longer time must be allowed for the attainment of equilibrium. The experimental apparatus consisted of a vertical tube, the upper portion of which was heated while the lower portion was kept at a low temperature.

Soret's latest experiments lend a quantitative support to our analogy. As with gases, it is to be expected that when the isotonic state is produced, the solution will exist in equilibrium ; and as the osmotic pressure is proportional to concentration and to absolute temperature, the isotonic state of different portions of the solution will occur when the product of the two (absolute temperature and concentration) are equal. If we therefore calculate, on this basis, the concentration of the warmer part of the solution from data obtained with the colder, the values compare with those found as follows :—

1. *Solution of Copper Sulphate.*—The portion cooled to 20° contained 17·332 per cent. The hot portion at 80° should contain 14·3 per cent. ; found, 14·03 per cent.

2. The portion cooled to 20° contained 29·867 per cent. The portion at 80° should contain 24·8 per cent. ; found, 23·871 per cent.

It must be stated that previous experiments by Soret gave less favourable results ; yet perhaps too much importance

should not be attached to them, owing to the difficulties of experiment.

## IV. Avogadro's *Law applied to Dilute Solutions.*

We have considered the changes produced in the osmotic pressure of solutions by alteration of temperature and con-centration, and attempted to exhibit the analogy between dilute solutions and gases, in relation to these two quantities It now remains to compare directly the two analogous quan-tities, gaseous pressure and osmotic pressure, in one and the same body. It is obvious that this analogy should hold with gases in solution ; and in actual fact it will be shown that, if Henry's law be taken into consideration, the osmotic pressure in solution is absolutely equal to the gaseous pressure, under similar conditions of temperature and concentration.

To prove this statement, we shall picture a reversible pro-cess by aid of semipermeable diaphragms, temperature being maintained constant ; and we shall again make use of the second law of thermodynamics, which in this case leads to the simple result that no work is transformed into heat, nor heat into work ; and hence the sum of all work done at different stages of the process is zero.

This reversible process may be conceived by means of two similar cylinders and pistons, like those already described. One contains a gas (A), say oxygen, and in contact with it a saturated aqueous solution of oxygen (B) (fig. 4). The wall *b c* allows only oxygen to pass, but no water ; the wall *a b*, on the other hand, water, but not oxygen; and it is in contact with water, E. A reversible process may be car-ried out by such an arrangement as follows :—By raising the two pistons (1) and (2), oxygen is

Fig. 4.

evolved from its aqueous solution as gas, while the water passes through *a b*; this change can proceed without altering the concentration of the solution. The only difference between the two cylinders is in the state of concentration of the solu-tions which they contain; we may explain the action thus :—The unit of weight of the substance in question occupies in the left-hand cylinder a volume v and V, and in the right-hand cylinder, $v + dv$ and $V + dV$; hence, in order that Henry's law may hold,

$$v : V = (v + dv) : (V + dV); \text{ hence } v : V = dv : dV.$$

If, now, the pressure, or osmotic pressure, as the case may be
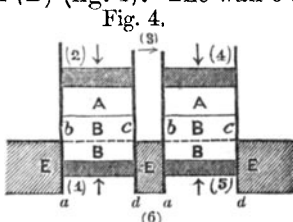
(supposing unit volume to contain unit mass), as regards gas and solution be P and p (which will afterwards be shown to be equal), then, from Boyle's law, the pressure in gas and solution will be $\dfrac{P}{v}$ and $\dfrac{p}{V}$ respectively.

Now let the pistons (1) and (2) be raised so as to liberate unit weight of gas from the solution, and increase the gaseous volume v by dv, in order to equalize its concentration with that of the gas in the left-hand vessel, and by depressing the pistons (4) and (5) let us redissolve the freshly liberated gas, and then reduce the volume of the solution $V + dV$ by the amount dV in the cylinder with semipermeable walls ; then the cycle is complete.

Work has been done in six separate ways ; let us number them (1), (2), (3), (4), (5), and (6). Now (2) and (4) are equal in amount, but opposite in sign, since they refer to change of volume v and $v + dv$ in opposite directions under pressures which are inversely proportional to the volumes. In similar manner the sum of (1) and (5) is zero ; so that the point requiring proof is that $(3) + (6) = 0$. Here (3) represents work done by the gas in increasing its volume by dv, under a pressure of $\dfrac{P}{v}$, therefore $(3) = \dfrac{P}{v} dv$; while (6) represents the work done by the solution, while it decreases in volume by dV, under a pressure of $\dfrac{p}{V}$, therefore $(6) = -\dfrac{p}{V} dV$. The statement is therefore

$$\frac{P}{v} dv = \frac{p}{V} dV ;$$

and as $v : V = dv : dV$, P must be equal to p, which was to be proved.

This conclusion, which will receive in the sequel ample confirmation, lends, on the one hand, support to Gay-Lussac's law in its application to liquids :—If gaseous pressure and osmotic pressure are at the same temperature equal to one another, then equal changes of temperature must affect both equally. On the other hand, this relation allows of a considerable extension of Avogadro's law, always provided that we may substitute the conception of osmotic pressure for gaseous pressure :—under equal osmotic pressures and at the same temperature, equal volumes of all solutions contain equal numbers of molecules; and, moreover, the same number of molecules which would be contained in an equal volume of a gas under the same conditions of temperature and pressure.

V. *General Expression for* Boyle's, Gay-Lussac's, *and*
Avogadro's *Laws for Solutions and Gases.*

The well-known formula expressing both Boyle's and Gay-Lussac's laws for gases,

$$PV = RT,$$

are, in so far as these laws are applicable to liquids, also applicable as regards osmotic pressure; with the reservation, also made in the case of gases, that the space occupied by the molecules must be so great that the actual volume of the molecules becomes negligible.

To include Avogadro's law in the above expression, Horstmann's suggestion (*Berl. Ber.* xiv. p. 1243) may be adopted, to express the molecular weight of the substance in kilograms; taking 2 kilos. of hydrogen, 44 kilos. of carbon dioxide, and so on. Then R in the above equation has always the same value; for, under equal conditions of temperature and pressure, these weights occupy the same volume. Calculating this value, and expressing the volume in cubic metres, and the pressure in kilograms per square metre, and choosing hydrogen gas at 0° and 760 millim. pressure as starting-point, then

$$P = 10333; \quad V = \frac{2}{0 \cdot 08956}; \quad T = 273; \quad R = 845 \cdot 05.$$

Hence the combined expression for Boyle's, Gay-Lussac's, and Avogadro's laws becomes

$$PV = 845\,T;$$

and this expression is applicable to solutions, substituting osmotic pressure for gaseous pressure.

We may give this equation even a simpler form, inasmuch as the number of calories equivalent to a kilogrammetre of work ($A = \dfrac{1}{J} = \frac{1}{423}$) stands in a very simple relation to R, viz. $AR = 2$ (in reality about one thousandth less). Hence we may choose the form

$$APV = 2T;$$

and this form has the great practical advantage that work, which will often be discussed in the following pages, receives a very simple expression, if calculated back to heat, measured in calories.

Let us next calculate the work, expressed in calories, when a gas or a solution, under constant pressure and temperature, expands V volumes; V volumes containing a kilogram-molecule. This is evidently 2T. It must be added that this

constant pressure is maintained only when the total volume of gas or solution is very great compared with V, or in cases of evaporation, where the vapour-pressure is at its maximum.

We shall also often have to express in calories the work done during isothermal expansion of the kilogram-molecule of a substance as gas, or in solution. If pressure falls a very small fraction ΔP, corresponding to a small increase of volume ΔV, the work done will be $AP\Delta V$, or $2\Delta T$.

VI. *First Confirmation of* Avogadro's *Law in its Application to Solutions.—Direct determination of Osmotic Pressure.*

It is to be expected that Avogadro's law, deduced as a consequence of Henry's law for solutions of gases, will not be restricted to solutions of substances which usually exist in a gaseous condition. This expectation has been realized, not merely from a theoretical, but from an experimental standpoint. Pfeffer's determinations of the osmotic pressure of solutions of sugar furnish a remarkable confirmation of this extension of the law.

Pfeffer's solution consisted of 1 gram of sugar dissolved in 100 grams of water ; one gram of the sugar therefore exists in about 100·6 cubic centim. of the solution. Comparing the osmotic pressure of this solution with the pressure of a gas (*e. g.* hydrogen) containing as many molecules in the volume, there are $\frac{2}{342}$ gram ($C_{12}H_{22}O_{11}=342$) in 100·6 cubic centim. Now one litre of hydrogen gas at $0°$ and 760 millim. pressure weighs 0·08956 gram ; and the above concentration is equivalent to 0·0581 gram per litre ; the pressure at $0°$ is 0·649 atmosphere, and at t, $0·649(1 + 0·00367\,t)$. Placing these results beside Pfeffer's, we obtain the following agreement :—

Temperature (t).	Osmotic pressure.	$0·649(1+0·00367\,t)$.
6·8	0·664	0·665
13·7	0·691	0·681
14·2	0·671	0·682
15·5	0·684	0·686
22·0	0·721	0·701
32·0	0 716	0·725
36·0	0·746	0·735

The directly determined osmotic pressure of a solution of sugar is thus seen to be equal to the pressure of a gas at the same temperature, containing the same number of molecules in unit volume as the sugar-solution.

Starting from cane-sugar, this relation can be calculated for other dissolved substances, such as invert sugar, malic acid, tartaric acid, citric acid, magnesium malate and citrate, all of

which, from de Vries' physiological researches (*Eine Methode zur Messung der Turgorkraft*, p. 512), exhibit equal osmotic pressure when they contain an equal number of molecules in a given volume.

VII. *Second Confirmation of* Avogadro's *Law in its Application to Solutions.—Molecular lowering of Vapour-pressure.*

The relation between osmotic pressure and the pressure of a vapour in contact with liquid, which is easily developed on thermodynamical principles, yields, from Raoult's recent observations, a satisfactory proof of the analogy under consideration.

We shall begin with a general law, of which the previous matter of this thesis is quite independent:—*Isotonism* (*i. e.* equal osmotic pressure—from ἴσος and τόνος, *stretching*) *in solutions made with the same solvent, implies equality of vapour-pressure.* This statement is easily proved by a reversible cycle, keeping temperature constant. Imagine two solutions exhibiting equal vapour-pressure, and introduce a small quantity of one in the state of vapour into the other in a reversible manner, *i. e.* by means of cylinder and piston. The vapour-pressures are equal, hence this transference takes place without expenditure of work ; and also, on restoring the original condition, no work is expended. But if the solvent be transferred back through a semipermeable diaphragm, separating the two solutions, then equal osmotic pressure must exist, else the transference could not take place without expenditure of energy.

If this fundamental conception be applied to dilute solutions, accepting the laws which have been explained in the preceding pages, the simple conclusion follows, that if a solvent contains equal numbers of molecules of dissolved substances, the vapour-pressure is the same. This is merely Raoult's law (*Comptes rendus*, lxxxvii. p. 167 ; xliv. p. 1431) of the constancy of molecular diminution of vapour-pressure, obtained by multiplying the relative diminution by the molecular weight of a one-per-cent. solution ; *i. e.* with the difference between the vapour-pressures of the solvent, before and after addition of dissolved substance. The equality of molecular diminution of vapour-pressure depends on the solutions containing equal numbers of molecules, a close proportionality between the lowering of the vapour-pressure and the concentration being assumed. With ether, for example, the value fluctuated between 0·67 and 0·74 (mean 0·71) for thirteen substances dissolved in it.

But this relation can be further developed. Different solutions may be compared with each other, and a second law may be deduced, which Raoult has also discovered experimentally. The following reversible process, consisting of two operations, is carried out with a very dilute solution of P per cent., at temperature T.

1. Remove, by use of cylinder with semipermeable wall, a portion of the solvent containing a kilogram-molecule (M) of the dissolved substance : here the total quantity of solution is supposed so great that no alteration of concentration occurs, and the expenditure of work is therefore 2T.

2. This quantity, $\dfrac{100\,M}{P}$ kilograms, of the solvent is returned as vapour ; it may be conceived as produced from the liquid by evaporation at its vapour-pressure ; then expanded till its pressure is equal to the vapour-pressure of the solution ; and finally liquefied in contact with the solution. The kilogram-molecule of the solvent (M′) will thus receive an expenditure of work of 2TΔ, where Δ represents the relative diminution of pressure ; and the $\dfrac{100\,M}{P}$ kilograms will receive $2T\Delta\dfrac{100\,M}{PM'}$. Here $\dfrac{\Delta}{P}\,M$ is Raoult's molecular diminution of pressure, which we shall term K ; employing this abbreviation, the expression becomes $\dfrac{200\,TK}{M'}$.

From the second law of thermodynamics, again, the algebraic sum of the work expended during this cycle at constant pressure must equal zero ; hence the work done by the solution during the first stage must equal the work done on it during the second ; and thus

$$2T = \frac{200\,TK}{M'} \; ; \; \text{or} \; 100\,K = M'.$$

This expression includes all Raoult's results. It expresses the fact, as stated above, that the molecular diminution of vapour-pressure is independent of the nature of the dissolved body ; and it also expresses, what Raoult found experimentally, that this diminution is independent of temperature. It also contains Raoult's second conclusion, that the molecular diminution is proportional to the molecular weight of the solvent, amounting to about one hundredth of the latter. This is seen from the following table :—

Solvent.	Molecular weight. (M').	Molecular diminution of vapour-pressure. (K).
Water	18	0·185
Phosphorous chloride . .	137·5	1·49
Carbon disulphide . . .	76	0·80
Carbon tetrachloride . .	154	1·62
Chloroform	119·5	1·30
Amylene	70	0·74
Benzene	78	0·83
Methyl iodide	142	1·49
Methyl bromide . . .	109	1·18
Ether	74	0·71
Acetone	58	0·59
Methyl alcohol	32	0·33

VIII. *Third Confirmation of* Avogadro's *Law in its Application to Solutions.—Molecular Depression of Freezing-point of Solvent.*

Here, again, a general law may be stated, connecting osmotic pressure with the freezing-point of a solution:— *Solutions in the same solvent, and of the same freezing-point, are isotonic at that temperature.* This statement admits, like the former, of proof by means of a reversible cycle ; but the solvent when returned is here in the condition of ice, not of vapour ; the inverse change is also brought about by means of a semipermeable diaphragm, and, as it cannot be accompanied by gain or loss of energy, isotonism must exist.

We shall apply the above statement to dilute solutions; and applying the relations previously described, the simple conclusion follows that solutions containing an equal number of molecules in equal volume, and which therefore, from Avogadro's law, are isotonic, also have the same freezing-point. This law has been actually discovered by Raoult, and is expressed by him as " normal molecular depression of freezing-point." It holds for the great majority of dissolved substances examined, and consists in the statement that the depression of freezing-point of a one-per-cent. solution, multiplied by the molecular weight of the dissolved substance, gives a constant product ; it is stated of solutions containing equal numbers of molecules in unit volume, assuming a close proportionality between concentration and lowering of the freezing-point. For an aqueous solution of nearly all organic bodies the constant product is about 18·5.

We can follow this relation still further, and, assuming Avogadro's law for solutions, deduce the above normal molecular depression of the freezing-point from other data. It bears a close relation to the heat of fusion of the solvent, as is shown by applying the second law of thermodynamics to a reversible cycle. Imagine a very dilute solution containing P per cent. of a dissolved substance, which has produced a depression of freezing-point, Δ ; the solution itself freezes at T, and its heat of fusion is W per kilogram.

1. By use of piston and cylinder with semipermeable walls, the solution is deprived at temperature T of that amount of the solvent in which a kilogram-molecule of the dissolved substance existed ; the amount of the solution is moreover so great that no appreciable change of concentration occurs, hence the work expended on it is 2T.

2. This quantity of solvent, $\dfrac{100\,M}{P}$, is then allowed to freeze at T by withdrawing $\dfrac{100\,MW}{P}$ calories; the solution and the solvent, now solid, are cooled through Δ degrees, and the solvent is now allowed to melt in contact with the solution, thereby absorbing the above quantity of heat. Finally, the temperature is raised Δ degrees.

During this reversible process $\dfrac{100\,MW}{P}$ calories rise from Δ to T, corresponding to an expenditure of energy equal to $\dfrac{100\,MW\Delta}{PT}$. In this expression, however, $\dfrac{M\Delta}{P}$ is the molecular depression of the freezing-point, which we may represent by the letter t ; the work done is therefore $\dfrac{100\,Wt}{T}$, and it was shown above to be equal to 2T. Hence the equation

$$\frac{100\,Wt}{T} = 2T \; ; \; \text{whence } t = 0 \cdot 02 \, \frac{T^2}{W}.$$

This theoretical deduction receives ample confirmation from experimental data. The following table exhibits the molecular depression of freezing-point experimentally determined by Raoult (*Annales de Chimie et de Physique*, [5] xxviii.; [6] xi.), along with the values calculated by means of the above formula :—

Solvent.	Freezing-point (T).	Heat of fusion (W).	$t = \dfrac{0 \cdot 02\, T^2}{W}$.	Raoult's molecular depression.
Water . . .	273	79	18·9	18·5
Acetic acid .	273 + 16·7	43·2*†	38·8	38·6
Formic acid .	273 + 8·5	55·6*†	28·4	27·7
Benzene . .	273 + 4·9	29·1†	53	50
Nitrobenzene.	273 + 5·3	22·3†	69·5	70·7

It may be added that, from the molecular depression of ethylene bromide (117·9), the hitherto unknown heat of fusion is found equal to 13 ; and Mr. Pettersson, at my request, having experimentally determined this constant, obtained the number 12·94.

IX. *Application of* Avogadro's *Law to Solutions.—The Law of* Guldberg *and* Waage.

Having discussed the physical aspect of this problem in order to furnish as many proofs as possible of the correctness of its treatment, it now remains to apply it to chemical facts.

The most evident application of Avogadro's law in reference to solutions is to the determination of the molecular weights of dissolved substances. This has already been attempted ; but here it is not the pressure which requires measurement, as with gases, when the molecular weight is deducible from volume, pressure, and temperature ; with solutions the osmotic pressure must be measured, and as yet the practical method is wanting. Yet this difficulty may be avoided by substituting for a determination of pressure that of the related values ; as, for example, the diminution of vapour-pressure, or the depression of the freezing-point. This proposal is Raoult's. He divides the reduction of vapour-pressure of water containing one per cent. of dissolved substance into 0·185 parts, or the observed depression of freezing-point into 18·5 parts ; and this method is comparable in respect of accuracy with determinations of the density of gases, and is in itself a strong presumption of the accuracy of Avogadro's law in its application to gases.

It is still more remarkable that the law of Guldberg and Waage, so generally accepted for solutions, can be evolved from the above laws regulating the behaviour of dilute solutions. Again, a reversible cycle at constant temperature must be imagined, which can be conceived for solutions equally well with gases, by means of semipermeable diaphragms.

* Berthelot, *Essai de Mécanique Chimique.*
† Pettersson, *Journ. f. prakt. Chem.* [2] xxvi. p. 129.

Let there be two systems of gaseous or dissolved substances in equilibrium, which may be expressed by the following symbols :—

$$a_{\prime}' M_{\prime}' + a_{\prime}'' M_{\prime}'' + \&c. \rightleftarrows a_{\prime\prime}' M_{\prime\prime}' + a_{\prime\prime}'' M_{\prime\prime}'' + \&c.,$$
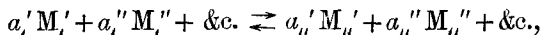
where a denotes the number of molecules, and M the formula. This equilibrium exists in two different vessels, A and B, at the same temperature but at different concentrations, shown by the partial pressure, or by the osmotic pressure which each of the bodies exerts. Let these pressures be in vessel A, $P_{\prime}' P_{\prime}'' \ldots P_{\prime\prime}' P_{\prime\prime}''$ &c.; and in B greater than these by $dP_{\prime}'$ $dP_{\prime}'' \ldots dP_{\prime\prime}' dP_{\prime\prime}'' \ldots$ &c.

The reversible cycle consists in introducing into A that amount in kilograms expressed by the first symbol of the first system, while the second is removed in equivalent amount : both systems have here the concentrations which exist in A (fig. 5). This change is accomplished by causing the entry or exit of each of the substances in question by means of its own cylinder and piston, which is separated from A by a diaphragm permeable to that body alone. If they are in solution, then the cylinders possess a semipermeable wall, and are surrounded by the solvent.
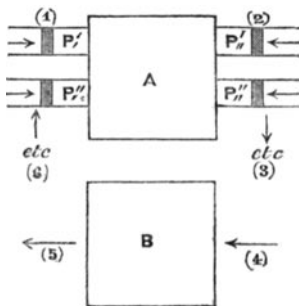
When this has been done, each constituent of the two systems has undergone such a change of concentration that it is now equal to that in B ; and, as before, the work done per kilogram-molecule equals $2\Delta T$, where Δ represents a minute fraction of the pressure, and is here $\dfrac{dP}{P}$; for the amounts here in question it is $2aT\dfrac{dP}{P}$.

Fig. 5.

By making use of the vessel B, the second system, which has just been evolved, is now converted into the first, but of concentration as in B, proceeding as just described ; and by suitable alteration of volume it is finally changed into its original state, as it at first existed in A.

As no change of temperature has occurred, the algebraic sum of all these operations is zero, as is seen from the numbers; it is thought unnecessary to interpret them, as they refer to the operations in the order in which they were carried out :—

$$(1) + (2) + (3) + (4) + (5) + (6) = 0.$$

Now (1) and (5) refer to operations opposite in sign on the same substances, with the same mass, at the same temperature; hence $(1) + (5) = 0$. And for similar reasons, $(2) + (4) = 0$; whence $(3) + (6) = 0$.

This conclusion leads directly to Guldberg's and Waage's law.

The work expressed by (3) is from that law $\Sigma 2a_{\prime\prime} T \dfrac{d\mathrm{P}_{\prime\prime}}{\mathrm{P}_{\prime\prime}}$, and (6) is $\Sigma 2a_\prime T \dfrac{d\mathrm{P}_\prime}{\mathrm{P}_\prime}$; hence it follows that

$$\Sigma\left(2a_{\prime\prime} T \frac{d\mathrm{P}_{\prime\prime}}{\mathrm{P}_{\prime\prime}} - 2a_\prime T \frac{d\mathrm{P}_\prime}{\mathrm{P}_\prime}\right) = 0, \text{ or } \Sigma\left(a_{\prime\prime} \frac{d\mathrm{P}_{\prime\prime}}{\mathrm{P}_{\prime\prime}} - a_\prime \frac{d\mathrm{P}_\prime}{\mathrm{P}_\prime}\right) = 0.$$

By integrating,

$$\Sigma(a_{\prime\prime} \log \mathrm{P}_{\prime\prime} - a_\prime \log \mathrm{P}_\prime) = \text{constant};$$

and here P is proportional to the concentration, or to the active mass C ; so that C may be substituted without altering the equation :—

$$\Sigma(a_{\prime\prime} \log \mathrm{C}_{\prime\prime} - a_\prime \log \mathrm{C}_\prime) = \text{constant}.$$

This is the logarithmic form of Guldberg's and Waage's formula.

X. *Deviation from* Avogadro's *Law in Solutions.— Variations in* Guldberg *and* Waage's *Law.*

We have attempted to show the connexion between Guldberg and Waage's law and the laws of Boyle, Henry, Gay-Lussac, and Avogadro, as applied to liquids ; as applied to gases, the truth of Guldberg and Waage's law has been long proved from thermodynamical considerations.

It remains to develop further the laws of chemical equilibrium, and, first, to investigate more closely the limits of applicability of the three fundamental principles from which Guldberg and Waage's law has been deduced.

So long as " ideal solutions " are under consideration, there exists strict analogy between gases and solutions ; and just as there are deviations from Avogadro's law in the case of gases, so we may expect to find them with solutions. As, for example, the pressure of the vapour of ammonium chloride was found to be too great to be accounted for by Avogadro's law, so the osmotic pressure is in many cases abnormal ; and as the high pressure in the first case is due to dissociation into ammonia and hydrogen chloride, it may be conceived that similar dissociation occurs in solutions. It must, indeed, be acknowledged that deviations are much more frequent with solutions than with gases, and occur often with bodies the

dissociation of which, under ordinary circumstances, does not appear probable; in aqueous solution, for example, the majority of salts as well as the stronger acids and bases undergo dissociation; and hence Raoult did not discover the existence of so-called normal molecular depression of freezing-point and lowering of vapour-pressure until he investigated organic compounds; their behaviour is almost without exception regular. For these reasons it may have appeared daring to begin by giving prominence to Avogadro's law in its application to solutions; and I should have shrunk from this course had not Arrhenius pointed out to me the probability that salts, and analogous bodies, decompose on solution into their ions; in fact, substances which obey Avogadro's law are, as a rule, non-conductors, suggesting that in such cases no dissociation into ions occurs; and further experimental proof exists for other liquids, since by Arrhenius's assumption the deviations from Avogadro's law are calculable from the conductivity.

However this may stand, an attempt is made in the following pages to take account of such deviations from Avogadro's law, and, by help of the application of Boyle's and Gay-Lussac's laws to solutions, to develop Guldberg's and Waage's formula so far as is possible.

The change in the expressions given above caused by these deviations is easily sketched.

The general expression for Boyle's, Gay-Lussac's, and Avogadro's laws, shown on p. 90, is

$$APV = 2T;$$

and this changes, if pressure is i-times that of this equation, into

$$APV = 2\,i\,T.$$

Hence, in a reversible cycle, the work will be i-times that previously done; this alteration is easily applied to the former statement of Guldberg's and Waage's formula. Recurring to the final stage of the cycle described on p. 97,

$$(3) + (6) = 0,$$

the work corresponding to (3) and (6), which were formerly $\Sigma 2a_{{\scriptscriptstyle //}} T \dfrac{d\mathrm{P}_{{\scriptscriptstyle //}}}{\mathrm{P}_{{\scriptscriptstyle //}}}$, and $-\Sigma 2a_{{\scriptscriptstyle /}} T \dfrac{d\mathrm{P}_{{\scriptscriptstyle /}}}{\mathrm{P}_{{\scriptscriptstyle /}}}$, is now increased i-times; hence the equations become

$$\Sigma\left(a_{{\scriptscriptstyle //}} i_{{\scriptscriptstyle //}} \frac{d\mathrm{P}_{{\scriptscriptstyle //}}}{\mathrm{P}_{{\scriptscriptstyle //}}} - a_{{\scriptscriptstyle /}} i_{{\scriptscriptstyle /}} \frac{d\mathrm{P}_{{\scriptscriptstyle /}}}{\mathrm{P}_{{\scriptscriptstyle /}}}\right) = 0;$$

and on integration,

$$\Sigma(a_{{\scriptscriptstyle //}} i_{{\scriptscriptstyle //}} \log \mathrm{P}_{{\scriptscriptstyle //}} - a_{{\scriptscriptstyle /}} i_{{\scriptscriptstyle /}} \log \mathrm{P}_{{\scriptscriptstyle /}}) = \text{constant.}$$

And introducing the concentration, or the active mass C, instead of the pressure proportional to it,

$$\Sigma(a_{\prime\prime}i_{\prime\prime} \log C_{\prime\prime} - a_{\prime}i_{\prime} \log C_{\prime}) = \text{constant.}$$

This is Guldberg's and Waage's law in a logarithmic form, differing from the former statement only by the introduction of the value i.

It remains to be shown that in this new form it agrees better with experimental results; and as a knowledge of the correct value of i is necessary, we must deal with aqueous solutions, for sufficient experimental data are to be had only with such.

XI. *Determination of* i *for Aqueous Solutions.*

As Avogadro's law has been proved for solutions by four separate lines of argument, there are four ways in which the deviations, *i. e.* the values of i, may be determined. But that one which depends on the lowering of the melting-point has been so thoroughly proved experimentally that we shall confine ourselves to its use.

Reverting to the cycle which, on p. 95, was employed to prove the applicability of Avogadro's law to solutions, the relation was found :—

$$\frac{100 \ Wt}{T} = 2T,$$

where the second term refers to the work done in removing or adding that amount of the solvent in which a kilogram-molecule of the substance was dissolved; that term must therefore be multiplied by i :—

$$\frac{100 \ Wt}{T} = 2i T.$$

In this manner a simple means of determining the value of i is apparent. The value of i is from the above equation proportional to t, *i. e.* to the molecular depression of temperature, for the other data (T=absolute melting-point, W=heat of fusion of solvent) are constant. Now 18·5 is the molecular depression for cane-sugar, which from p. 91 is seen to follow Avogadro's law accurately ; hence $i=1$; and for other bodies i is their respective depressions divided by 18·5. Almost identical results are arrived at by using in the above equation, instead of T and W, the values for ice, viz. 273 and 79 ; they will therefore be employed in the following calculations.

XII. *Proof of the Modified Law of* Guldberg *and* Waage.

In employing the relation proposed for the purpose of comparison with the results of Guldberg and Waage's formula,

it is necessary to mention the different forms which it has assumed during the years since its discovery. We shall first give this relation a simple expression in which Guldberg and Waage's conceptions may be included, viz. :—

$$\Sigma ai \log C = K. \quad \ldots \ldots \quad (1)$$

This differs from the one given on p. 100 merely in that the terms representing the components of both systems have had their signs changed. The original expression of the Norwegian investigators is closely analogous (*Christiania Videnskabs Selskabs Forhandlingar*, 1864) :—

$$\Sigma k \log C = K . \quad \ldots \ldots \quad (2)$$

except that k has to be determined for each constituent in question by observation of the equilibrium of the system.

As Guldberg and Waage (*Études sur les affinités chimiques*, 1867) repeatedly found the coefficient k equal to 1, they simplified their equation thus :—

$$\Sigma \log C = K. \quad \ldots \ldots \quad (3)$$

In their last treatise, however (*Jour. für prakt. Chem.* xix. p. 69), they introduce the change that the number of molecules a must also be taken account of, and consequently they approximate their formula to that deduced for gases on thermodynamical grounds, thus :—

$$\Sigma a \log C = K ; \quad \ldots \ldots \quad (4)$$

We have taken this last expression as their final formula.

The Norwegian investigators maintained this simple formula, with whole numbers as coefficients, even for solutions ; but Lemoine has lately revived the original formula (2) in order to represent the results of Schlösing's investigations on the solubility of calcium carbonate in water containing carbon dioxide, with constants hereafter to be determined, which are, however, not whole numbers ; for if whole numbers be employed, it is impossible to reconcile fact with theory.

In view of this uncertainty, the formula which we have suggested has this advantage, that the coefficients which occur in it are *à priori* determined, and its truth can at once be decided by experiment. It will in fact appear that in the instances studied by Guldberg and Waage the simple form which they recommend is completely confirmed ; and that such simplification is in most cases admissible confirms, moreover, the validity of Avogadro's law in its application to solutions. On the other hand, the results of Schlösing's investigation, prominently alluded to by Lemoine, cannot be

simply expressed, and require the same fractional coefficients which Schlösing himself arrived at.

Before proceeding to this investigation, it is necessary to include cases where partially insoluble bodies are present: this is easily done ; they may be included in the formulæ given above, remembering that such bodies exist in solution up to its saturation-point, and are therefore present with constant concentration. All concentrations depending on this may, therefore, be removed from the first term of the above equation to the second, without affecting the constancy of the latter. Everything remains the same, except that in the first term only the dissolved bodies need be considered.

1. We shall first examine Guldberg and Waage's observations. The first case they studied was that expressed by the equation

$$BaCO_3 + K_2SO_4 \rightleftharpoons BaSO_4 + K_2CO_3 ;$$
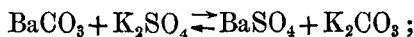
and they found, according to their simplified formula, that

$$\log C_{K_2SO_4} - \log C_{K_2CO_3} = K.$$

The relation given by our equation is almost identical, for, for K_2SO_4, $a = 1$ and $i = 2\cdot11$, and for K_2CO_3, $a = 1$ and $i = 2\cdot26$; hence

$$\log C_{K_2SO_4} - 1\cdot07 \log C_{K_2CO_3} = K.$$

A similar agreement exists with sodium carbonate, for then the values of i for Na_2SO_4 and Na_2CO_3 are $1\cdot91$ and $2\cdot18$ respectively ; hence

$$\log C_{Na_2SO_4} - 1\cdot14 \log {}_{Na_2CO_3} = K.$$

2. This result, expressed in what is almost a whole number, cannot be expected in the above-mentioned experiment of Schlösing (*Comptes rendus*, lxxiv. 1552 ; lxxv. 70). There the subject of experiment was the solubility of calcium carbonate in water containing carbonic acid, and the state of equilibrium is expressible by the following statement :—

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2.$$
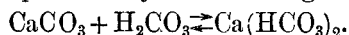
We should expect that, as $i = 1$ for carbon dioxide, that i should $= 2\cdot56$ for calcium hydrogen carbonate :—

$$0\cdot39 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K ;$$

and Schlösing found : —

$$0\cdot37866 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K.$$

Similar experiments with barium are equally satisfactory ; the value of i for barium hydrogen carbonate is $2\cdot66$, and the following results are calculated :—

$$0\cdot376 \log C_{H_2CO_3} - \log C_{Ba(HCO_3)_2} = K.$$

The experimental result is

$$0.38045 \log C_{H_2CO_3} - \log C_{Ba(HCO_3)_2} = K.$$

3. Turning to Thomsen's investigation on the action of sulphuric acid on sodium nitrate in solution (Thomsen's *Thermochemische Untersuchungen*, i.), we find a similar agreement.

The reaction may be formulated thus :—

$$Na_2SO_4 + HNO_3 \rightleftharpoons NaHSO_4 + NaNO_3 ;$$

and Guldberg and Waage's relation requires

$$\log C_{Na_2SO_4} + \log C_{HNO_3} - \log C_{NaHSO_4} - \log C_{NaNO_3} = K.$$

Now

$i_{Na_2SO_4} = 1.91$; $i_{HNO_3} = 1.94$; $i_{NaHSO_4} = 1.88$; and $i_{NaNO_3} = 1.82$; and the equation becomes

$$1.05 \log C_{Na_2SO_4} + 1.06 \log C_{HNO_3} - 1.03 \log C_{NaHSO_4} - \log C_{NaNO_3} = K,$$

which is almost identical.

If we express the relation thus :—

$$Na_2SO_4 + 2HNO_3 \rightleftharpoons H_2SO_4 + 2NaNO_3,$$
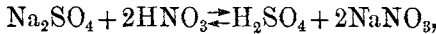
Guldberg and Waage's formula becomes

$$\log C_{Na_2SO_4} + 2 \log C_{HNO_3} - \log C_{H_2SO_4} - 2 \log C_{NaNO_3} = K ;$$

and we obtain :

$$\log C_{Na_2SO_4} + 2.03 \log C_{HNO_3} - 1.07 \log C_{H_2SO_4} - 1.91 \log C_{NaNO_3} = K ;$$

Again an almost absolute agreement.

4. Ostwald's investigation (*J. prakt. Chem.* [2] xix. p. 480) on the action of hydrochloric acid on zinc sulphide, according to the formula

$$ZnS + 2HCl \rightleftharpoons H_2S + ZnCl_2,$$
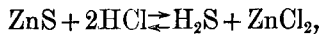
leads, when the following values are ascribed :

$$i_{HCl} = 1.98 ; i_{H_2S} = 1.04 ; i_{ZnCl_2} = 2.53$$

to the equation :—

$$3.96 \log C_{HCl} - 1.04 \log C_{H_2S} - 2.53 \log C_{ZnCl_2} = K.$$

It is evident that the concentrations of the sulphuretted hydrogen and the zinc chloride are equal, for only hydrochloric acid and zinc sulphide are initially present. The result is expressible by taking the volume V, in which a known amount of hydrochloric acid was dissolved, as the

initial concentration; and the fraction x to denote that portion which after contact with zinc sulphide has finally reacted, forming zinc chloride. Hence we have

$$3 \cdot 96 \log \frac{1-x}{V} - 3 \cdot 57 \log \frac{x}{V} = \text{const.};$$

and also

$$\frac{x}{(1-x)^{1 \cdot 11}} V^{0 \cdot 11} = \text{const.}$$

This function is really nearly constant:

| Volume (V).	Portion reacted (x).	$\dfrac{x}{(1-x)^{1 \cdot 11}} V^{0 \cdot 11}$
1	0·0411	0·043
2	0·038	0·0428
4	0·0345	0·0418
8	0·0317	0·0413

Similar experiments with sulphuric acid, where i for H_2SO_4 and $ZnSO_4$ is respectively 2·06 and 0·98, gave

$$\frac{x}{(1-x)^{1 \cdot 02}} V^{0 \cdot 02} = \text{const.};$$

and here also x is nearly a constant, as is seen from the following experimental numbers :—

Volume V.	Portion reacted (x).
2	0·0238
4	0·0237
8	0·024
16	0·0241

5. The experiments of Engel on the solubility of magnesium carbonate in water containing carbonic acid (*Comptes rendus*, c. pp. 352, 444) also deserve notice. The state of equilibrium is

$$MgCO_3 + H_2CO_3 \rightleftarrows Mg\,(HCO_3)_2\;;$$
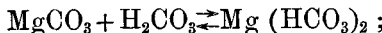
and our formula leads to the following relation, where $i = 2 \cdot 64$ for acid magnesium carbonate :—

$$0 \cdot 379 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

The number found was

$$0 \cdot 370 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

6. Other experiments by the same author on the simultaneous solubility of copper and ammonium sulphates (*Comptes rendus*, cii. p. 113), are shown by the reversible equation

$$CuSO_4 + (NH_4)_2SO_4 \rightleftarrows Cu\,(NH_4)_2(SO_4)_2.$$
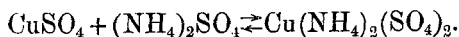
As the double salt was always partly undissolved, and as the values of i for $CuSO_4$ and for $(NH_4)_2SO_4$ are 0·98 and 2·0, we have the relation

$$0·49 \log C_{CuSO_4} - \log C_{(NH_4)_2SO_4} = K.$$

The number found is 0·438 $\log C_{CuSO_4}$.

7. In conclusion, we may notice Le Chatelier's experiments on the equilibrium between basic mercuric sulphate and sulphuric acid (*Comptes rendus,* xcvii. p. 1565);

$$Hg_3SO_6 + 2H_2SO_4 \leftrightarrows 3HgSO_4 + 2H_2O.$$
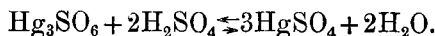
In this case the values of i for H_2SO_4 and $HgSO_4$ are 2·06 and 0·98, and we have

$$1·4 \log C_{H_2SO_4} - \log C_{HgSO_4} = K.$$

The found value is 1·58 $\log C_{H_2SO_4}$.

Generally speaking, therefore, such results show a very satisfactory agreement.

XIII. *On an Explanation of the Action of a Magnet on Chemical Action. By* HENRY A. ROWLAND *and* LOUIS BELL*.

IN the year 1881 Prof. Remsen discovered that magnetism had a very remarkable action on the deposition of copper from one of its solutions on an iron plate, and he published an account in the American Chemical Journal for the year 1881. There were two distinct phenomena then described—the deposit of the copper in lines approximating to the equipotential lines of the magnet, and the protection of the iron from chemical action in lines around the edge of the poles.   It seemed probable that the first effect was due to currents in the liquid produced by the action of the magnet on the electric currents set up in the liquid by the deposited copper in contact with the iron plate.   The theory of the second kind of action was given by one of us, the action being ascribed to the actual attraction of the magnet for the iron, and not to the magnetic state of the latter.   It is well-known since the time of Faraday that a particle of magnetic material in a magnetic field tends to pass from the weaker to the stronger portions of the field ; and this is expressed mathematically by stating that the force acting on the particle in any direction is proportional to the